Ferroelectric Polymers and Composites for Actuators and Sensors

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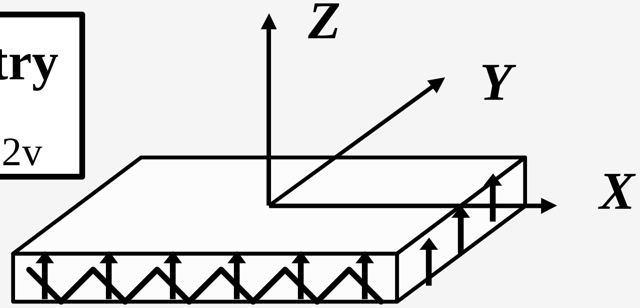
Classification of Piezoelectric Polymers

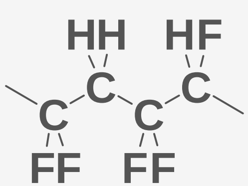
1. *Poled Polar Polymers*

Symmetry
$C_{\infty v}$, C_{2v}

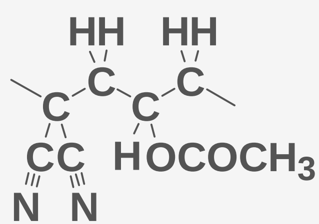


$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ p_3 \end{pmatrix}$$

VDF/TrFE



VDCN/VAc

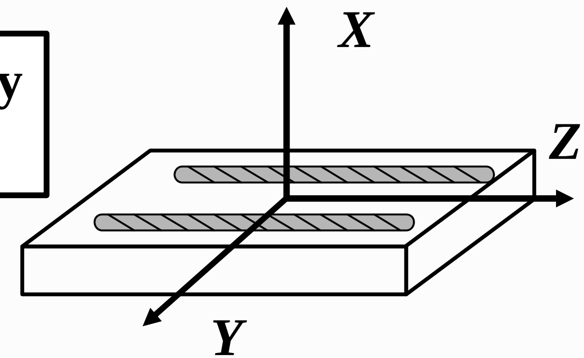


Odd Nylon

PZT/Polymer Composite

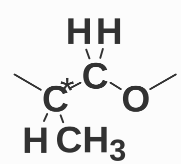
2.*Oriented Chiral Polymers*

Symmetry
$D_{¥}$, D_2

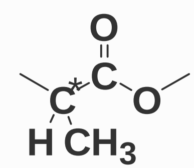


$$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

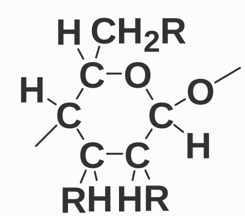
PPO



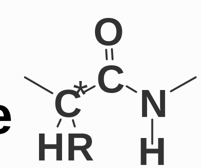
PLA



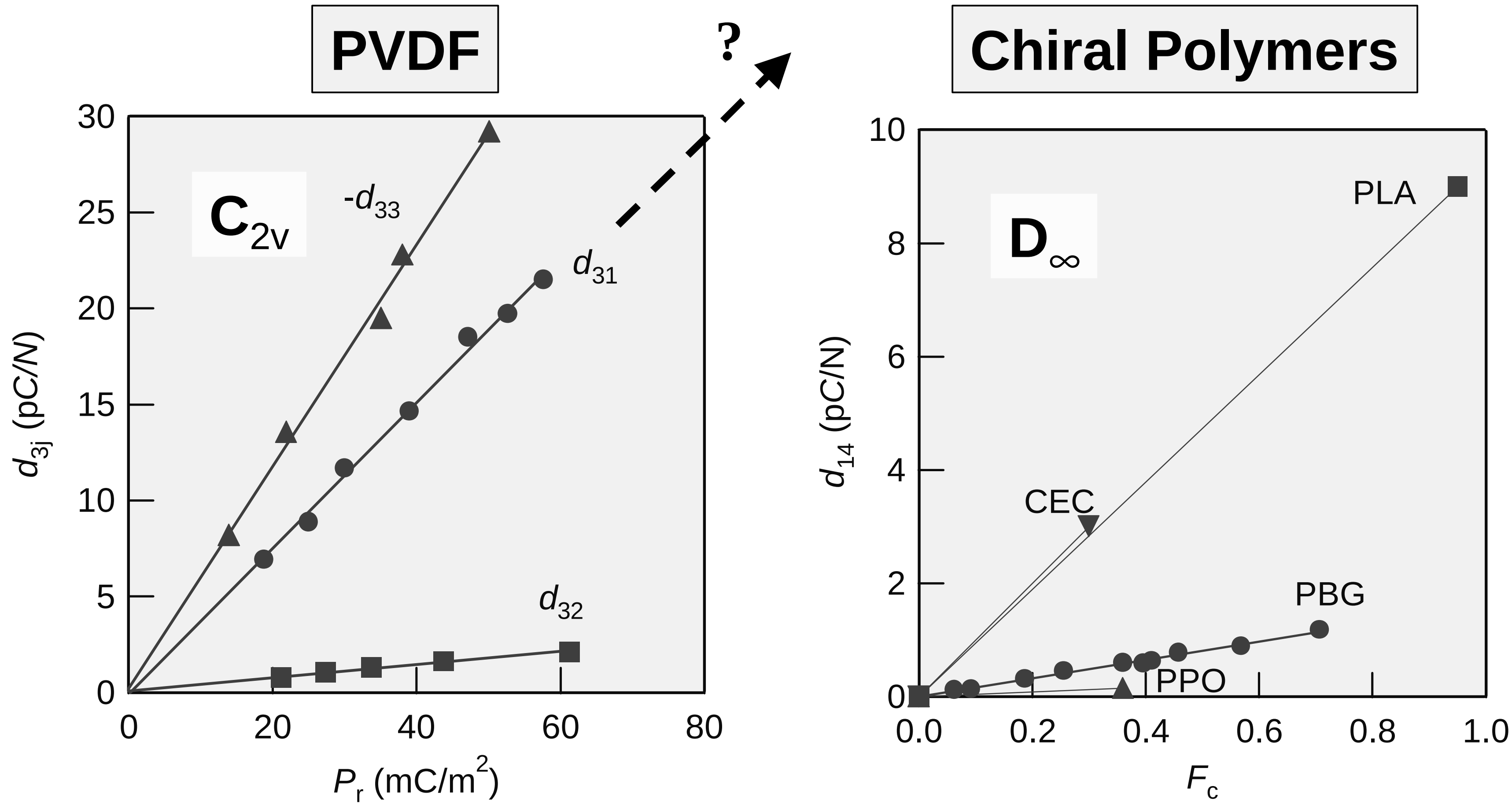
Cellulose



Polypeptide



Structure-Dependent Piezoelectric Constants of Oriented Polymer Films

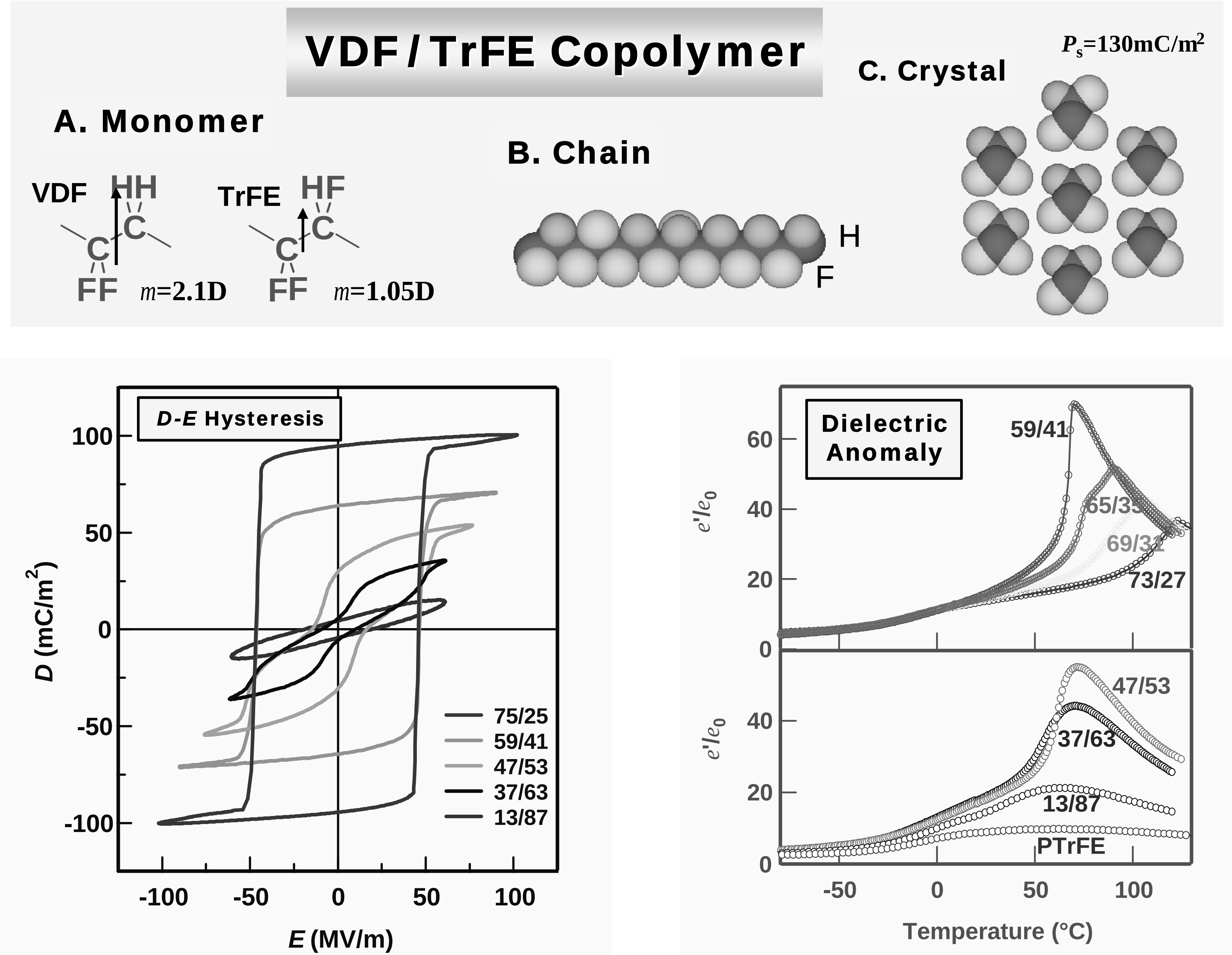


$$P_1 = \langle \cos q \rangle$$

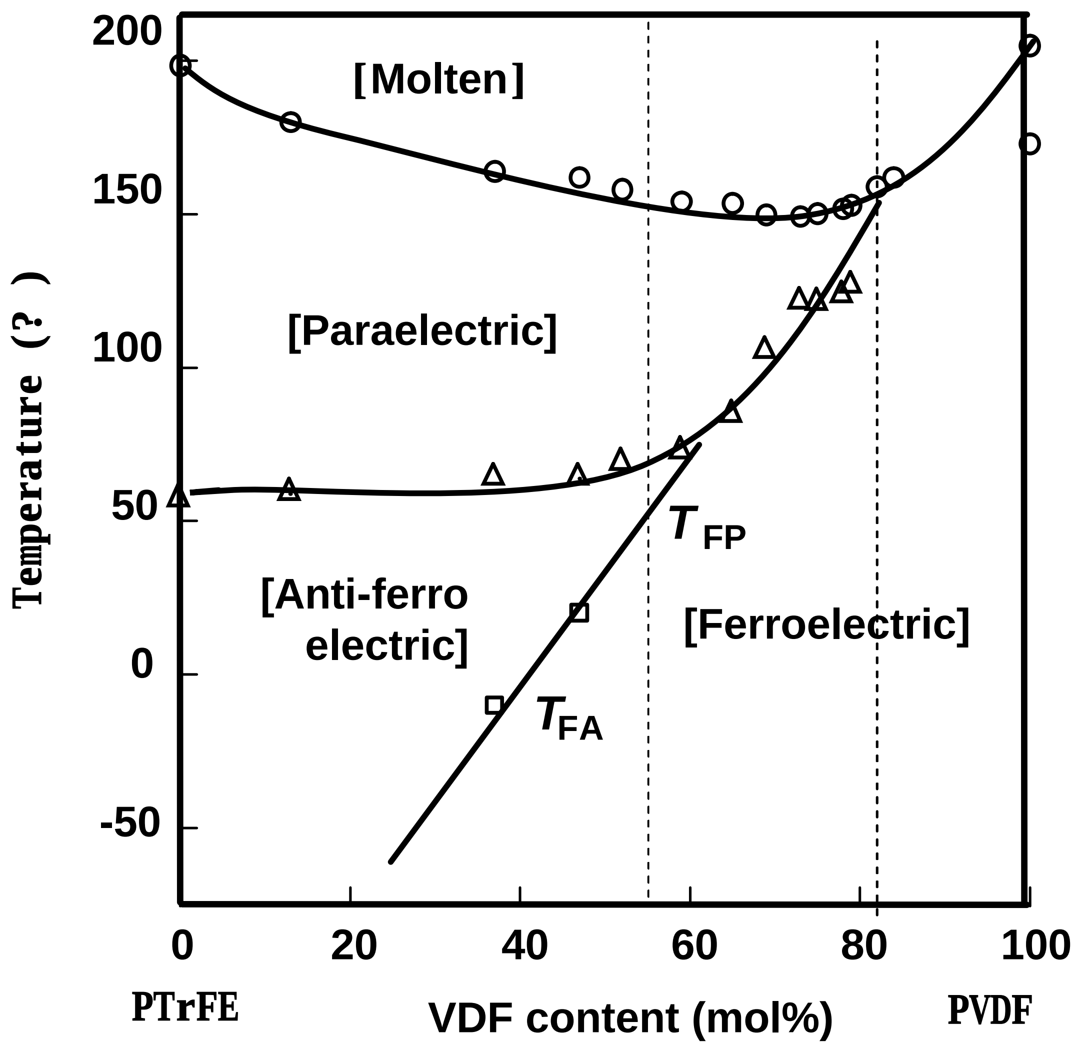
$$P_2 = \frac{1}{2}(3 \langle \cos^2 q \rangle - 1)$$

Dipole orientation

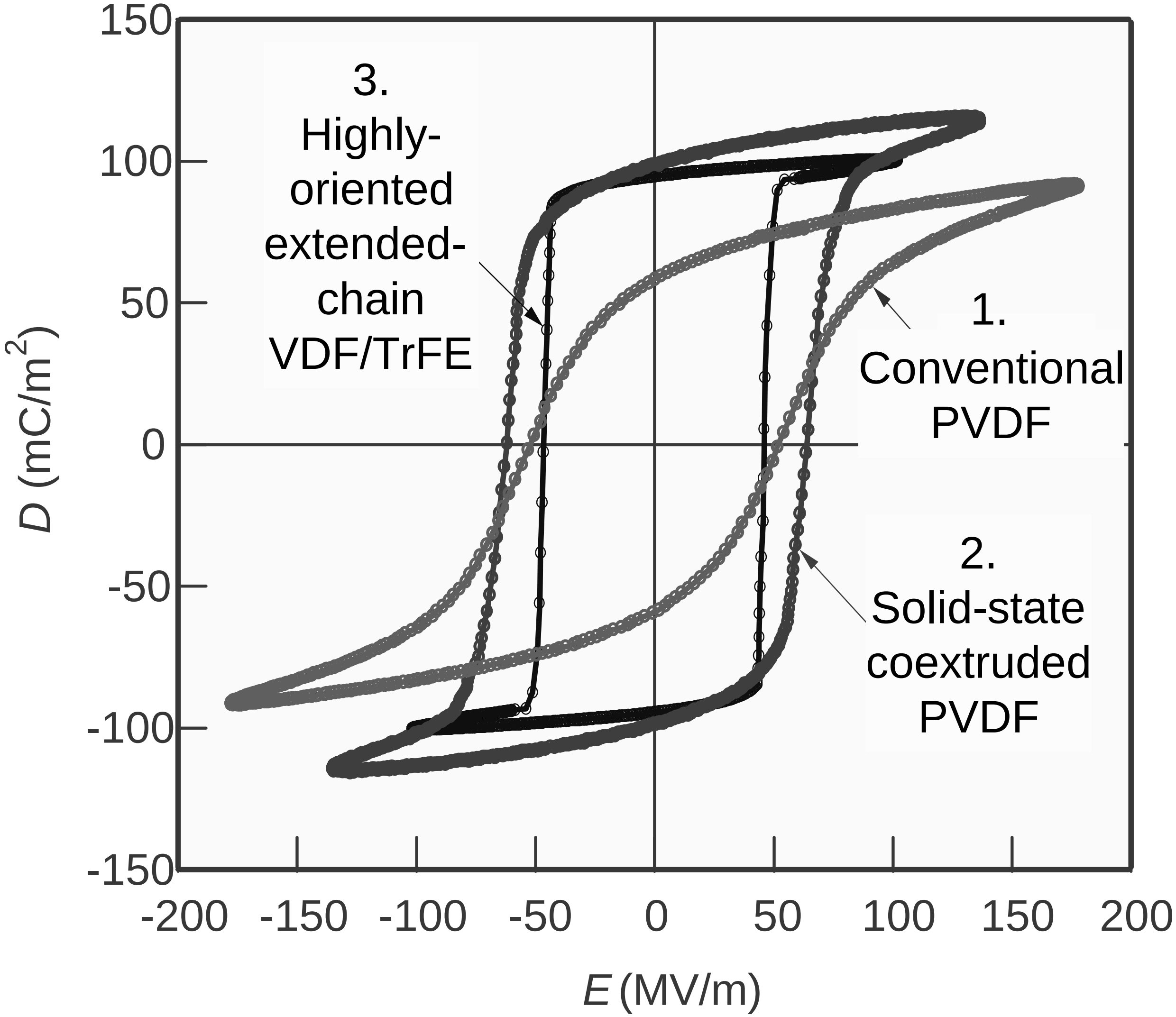
Chain orientation


VDF / TrFE Copolymer
A. Monomer
VDF
HH
C
C
FF
m=2.1D
TrFE
HF
C
C
FF
m=1.05D
B. Chain
H
F
C. Crystal
P_s=130mC/m^2
D-E Hysteresis
100
50
0
-50
-100
D (mC/m^2)
-100
-50
0
50
100
E (MV/m)
75/25
59/41
47/53
37/63
13/87
Dielectric Anomaly
e'/e_0
60
40
20
0
59/41
65/35
69/31
73/27
47/53
37/63
13/87
PTrFE
-50
0
50
100
Temperature (°C)

Phase Diagram of VDF/TrFE Copolymers



Improved-Performance of PVDF and VDF/TrFE Copolymer



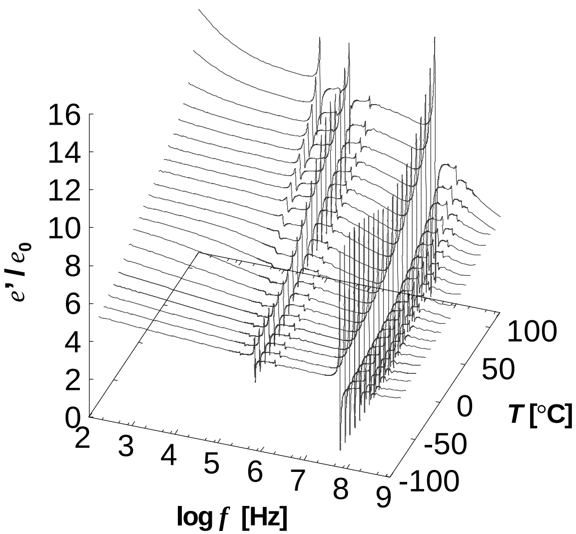
1. Conventional PVDF
   Uniaxial-drawn 4 times
   P_r=60mC/m^2
   k_{33}=0.14

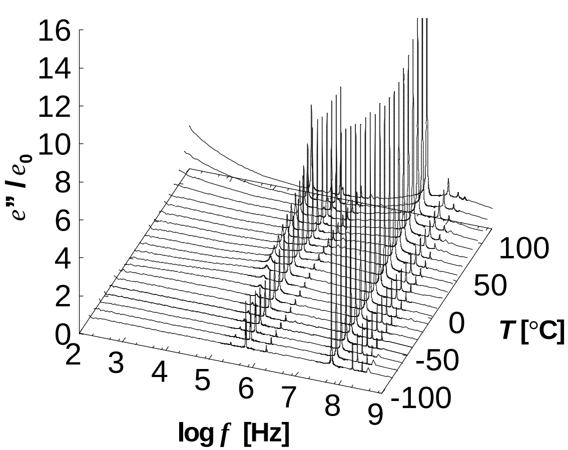
2. High Performance PVDF
   Solid-state coextruded
   P_r=100mC/m^2
   k_{33}=0.27

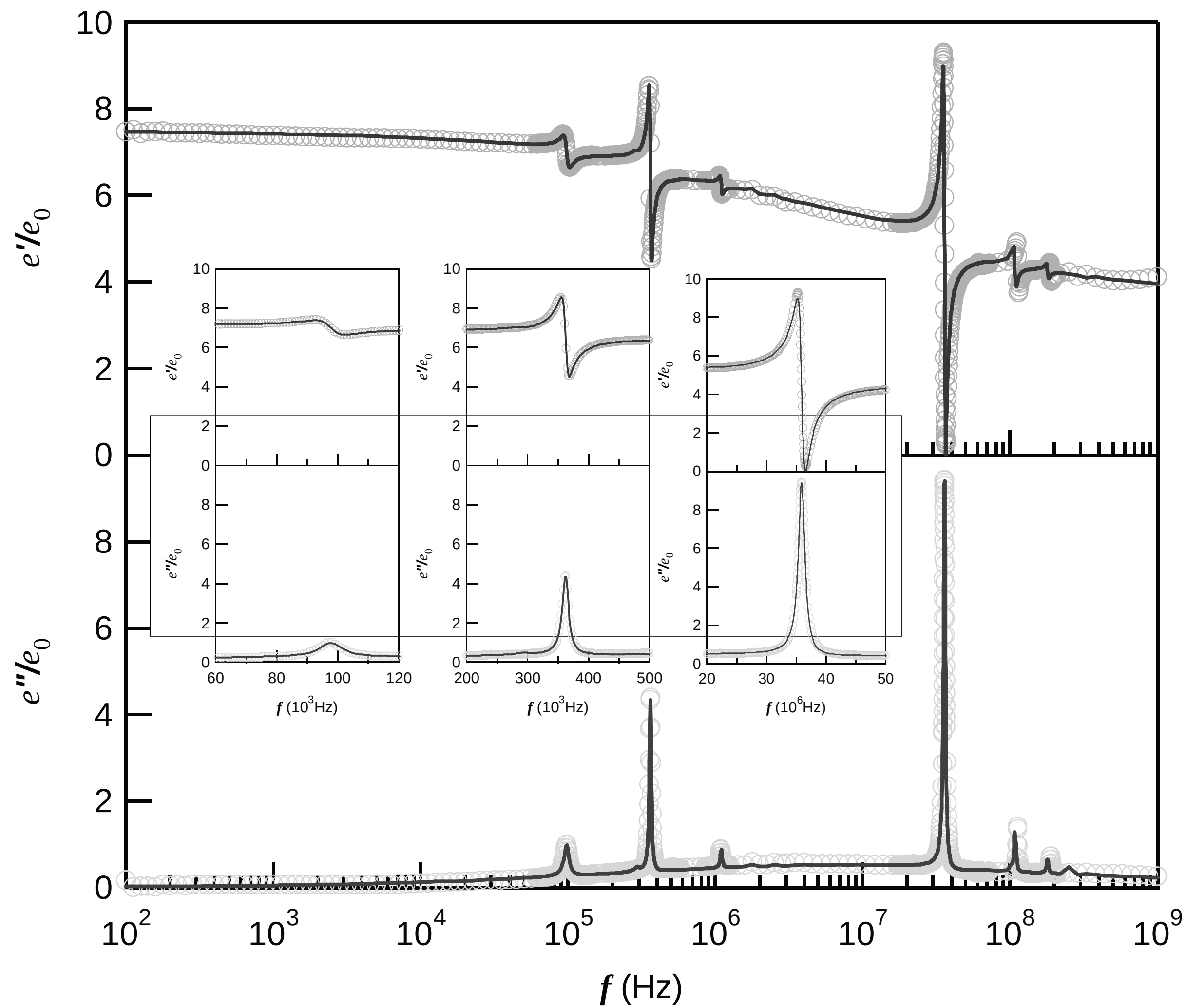
3. VDF(75)/TrFE(25)
   Uniaxially-drawn
   and annealed
   Highly-oriented
   extended-chain crystals
   P_r=100mC/m^2
   k_{33}=0.27

Piezoelectric Resonance in VDF/TrFE Copolymer

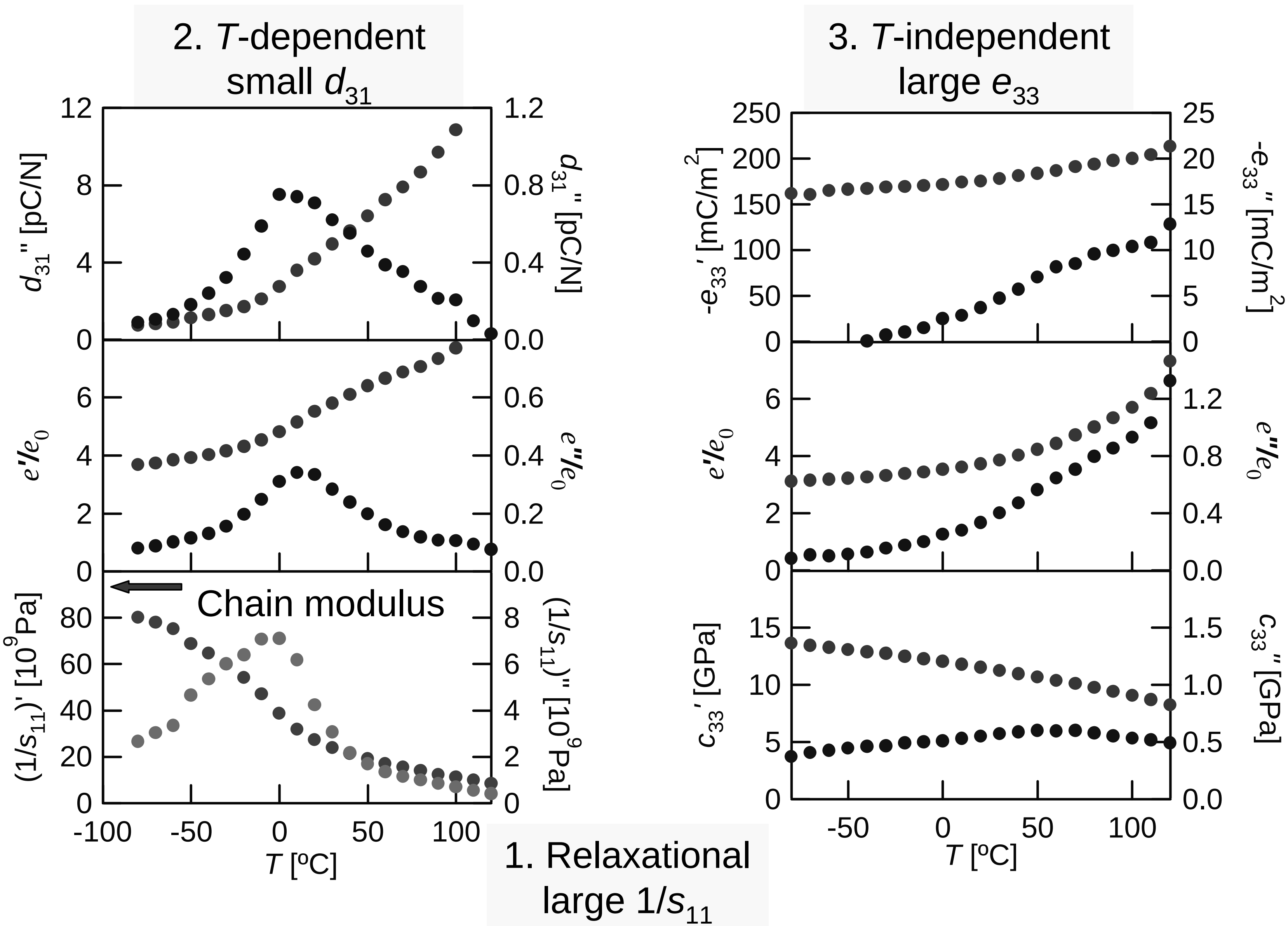
$$e^{*} = e^{S}\,\frac{\left(1+\dfrac{k_l^2}{1-k_l^2}\dfrac{\tan a_l f}{a_l}\right)\left(1+\dfrac{k_w^2}{1-k_w^2}\dfrac{\tan a_w f}{a_w}\right)}{1-k_t^2\,\dfrac{\tan a_t f}{a_t}}$$







Temperature Spectra of Elastic, Piezoelectric and Dielectric Constants of Extended-Chain-Crystal VDF(75) / TrFE(25) Film

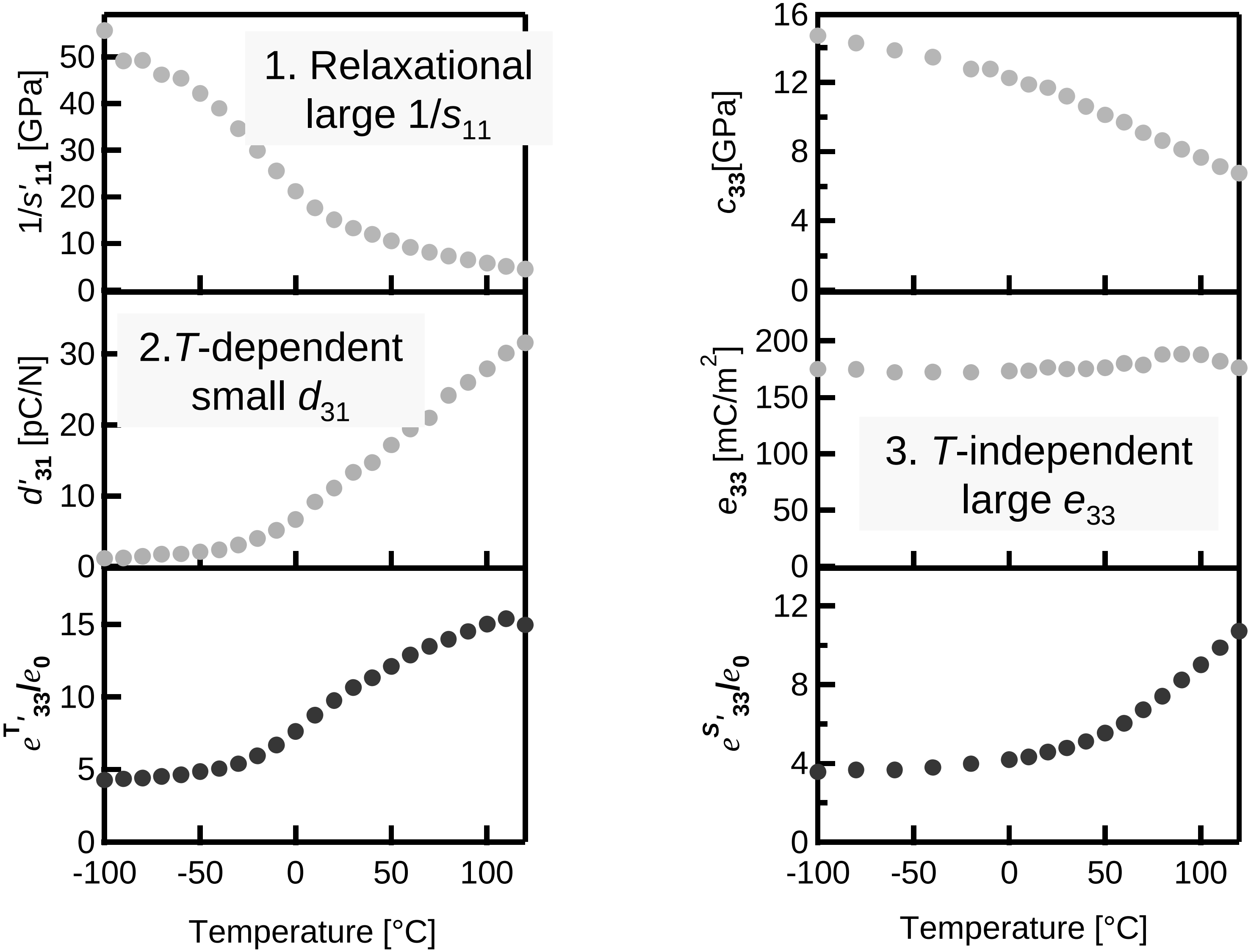


Thermo-Electro-Mechanical 22 Matrix Components of Highly-Oriented VDF(75)/TrFE(25) Copolymer Films with C_{2v} Symmetry at 20?

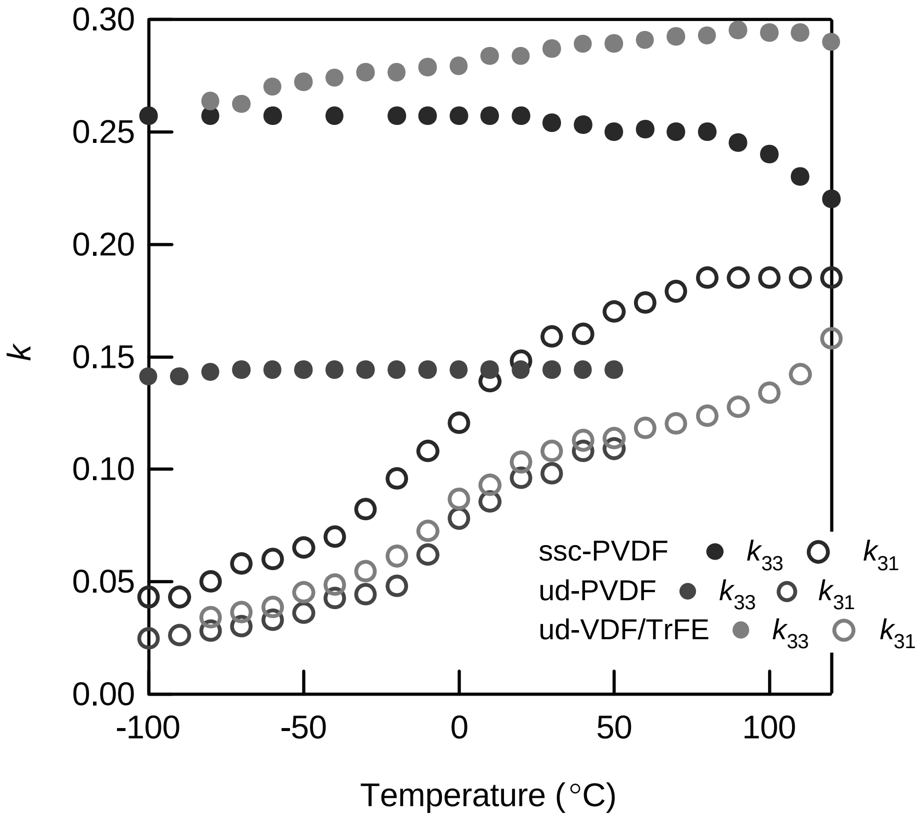
	X_1	X_2	X_3	X_4	X_5	X_6	E_1	E_2	E_3	T
x_1	40	-6	-21						4	50
x_2		15	-62						12	130
x_3		0	150						-29	90
x_4				400				-50		
x_5					450		-31			
x_6	s_{ij}					71				
D_1					d_{15}	0	5			
D_2				d_{24}				7		
D_3	d_{31}	d_{32}	d_{33}				e_{ik}/e_0		10	25
S	a_1	a_2	a_3						p_3	2.3

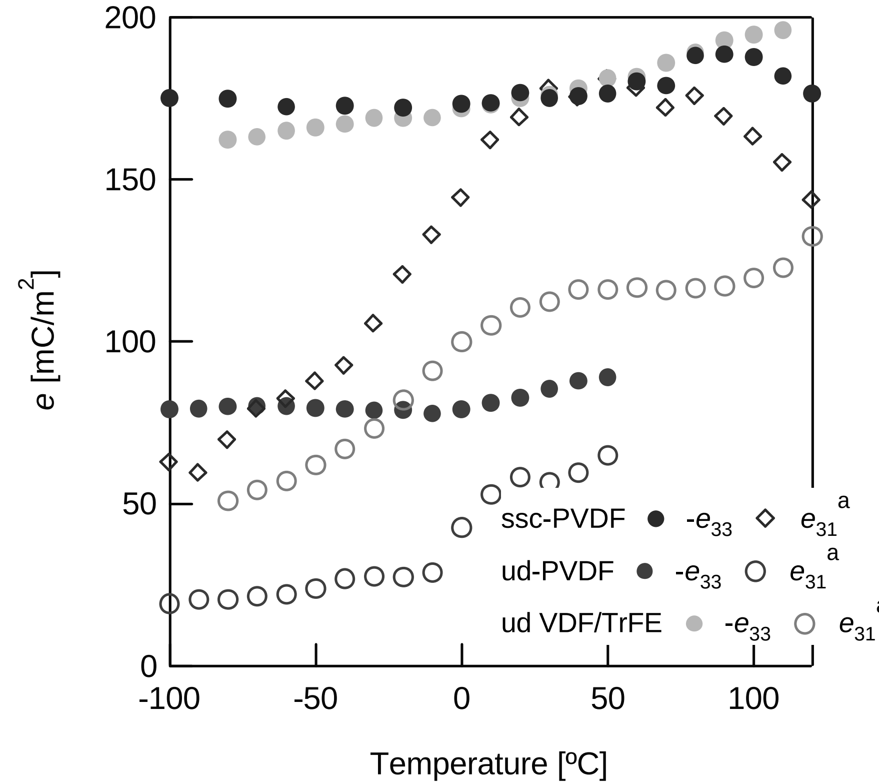
s_{jl} (nPa^{-1}), e_{ik}/e_0, C (MJ/m^{3}K), d_{ij} (pC/N), p_i (μC/m^{2}K), a_j (μK^{-1})

Temperature Spectra of Elastic, Piezoelectric and Dielectric Constants of Coextruded PVDF



Temperature Dependence of Electromechanical Coupling Coefficients and Piezoelectric Constants for PVDF and VDF/TrFE





Electromechanical Properties of Coextruded PVDF and Highly-Oriented VDF/TrFE at 20?

Materials	d_{31}(pC/N) k_{31}	$1/s_{11}^{E}$(GPa) e_3^{X}/e_0	e_{33}(mC/m^2) k_{33}	c_{33}^{D}(GPa) e_3^{x}/e_0	p_3(μC/m^{2}K) P_r(mC/m^2)
PVDF Conventional	16 0.10	4 10	-90 0.14	12 5	25 60
PVDF Coextruded	**11** **0.16**	**16** **10**	**-180** **0.27**	**12** **5**	**25** **100**
VDF(75)/TrFE(25) Highly-Oriented	**4** **0.11**	**28** **7**	**-185** **0.29**	**12** **4**	**25** **95**

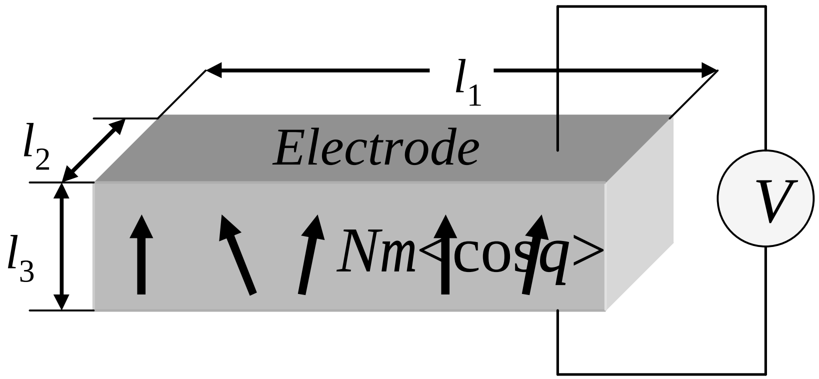
? *T*-independent large k_{33} and e_{33} associated with thickness change

? *T*-dependent <u>small</u> d_{31} originated in $e_{33}\,s_{31}$

? Large but relaxational Young's modulus reflecting extended-chain stiffness and chain motion

? Quantitative understanding of basic mechanisms

Mechanisms of Piezoelectricity in Ferroelectric Polymers



Experimental Data

P_r=100mC/m^2

e_{33}=-200mC/m^2

Polarization $$P_r = \frac{Nm\langle\cos q\rangle}{l_1 l_2 l_3}$$

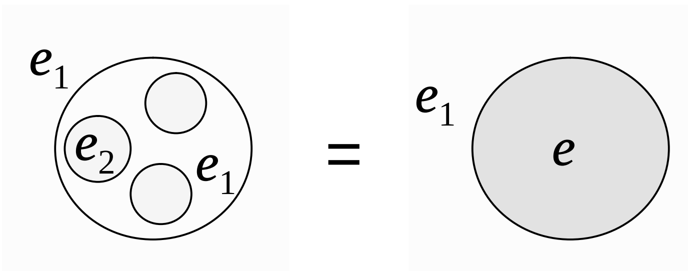
Charge on the Electrode $$Q = \frac{Nm\langle\cos q\rangle}{l_3}$$

Piezoelectric *e*-constant $$e_{33} = \frac{l_3}{l_1 l_2}\left(\frac{\partial Q}{\partial l_3}\right)_{V=0} = -P_r\left(1 - \frac{\partial \ln m}{\partial \ln l_3} - \frac{\partial \ln\langle\cos q\rangle}{\partial \ln l_3}\right)$$

Dimensional effect $$\left(-\frac{\partial \ln(1/l_3)}{\partial \ln l_3} = 1\right)$$

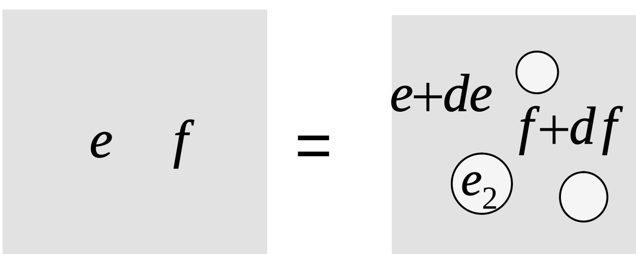
Remaining=1 $$\begin{pmatrix}\text{local field}\\ \text{dipole orientation}\end{pmatrix}$$

Two-Phase Spherical Dispersion System



$$\frac{e - e_1}{e + 2e_1} = f\,\frac{e_2 - e_1}{e_2 + 2e_1}$$

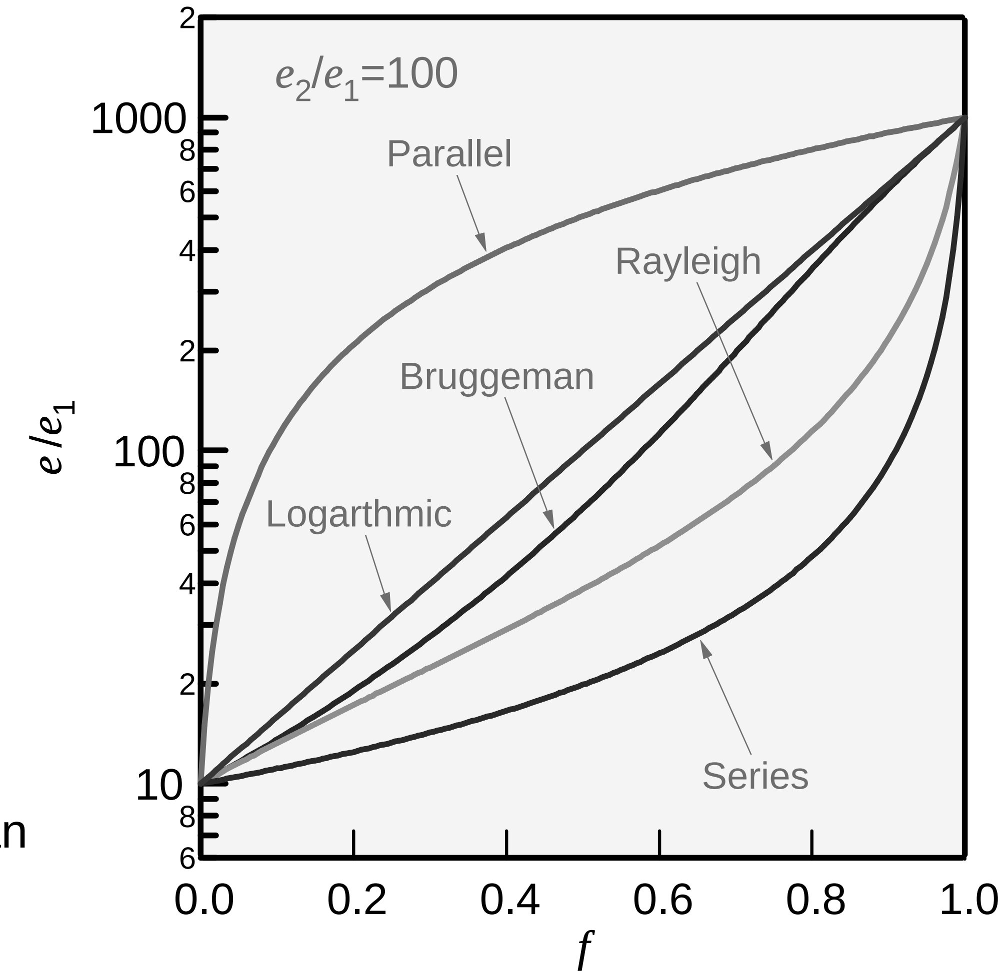
Rayleigh
(1892)



$$de = \frac{df}{1-f}\,\frac{e_2 - e}{e_2 + 2e}\,3e$$

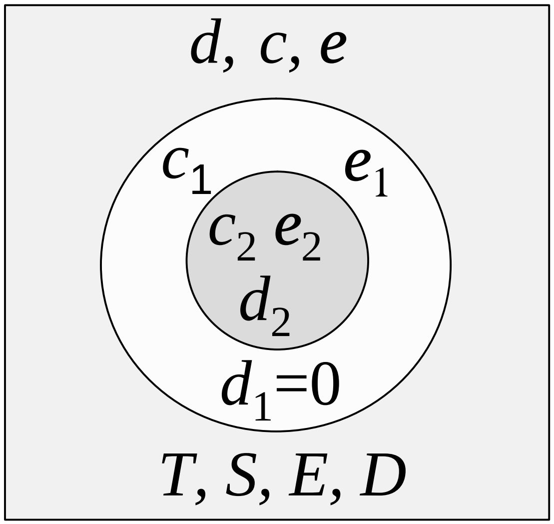
$$(1-f)\left(\frac{e}{e_1}\right)^{1/3} = \frac{e_2 - e}{e_2 - e_1}$$

Bruggeman
(1935)



Piezoelectric Mixing Law

Piezoelectric spherical inclusion in non-piezoelectric matrix



Piezoelectric constants

$$d = fL_E L_T d_2$$

$$e = fL_E L_S e_2$$

$$g = fL_D L_T g_2$$

$$h = fL_D L_S h_2$$

Dielectric permittivity

$$(1-f) = \frac{e_2 - e}{e_2 - e_1}\left(\frac{e}{e_1}\right)^{-1/3}$$

Elastic constant

$$(1-f) = \frac{c_2 - c}{c_2 - c_1}\left(\frac{c}{c_1}\right)^{-2/5}$$

Local field coefficients

Stress

$$L_T = \frac{T_2}{T} = \frac{c_2(c - c_1)}{fc(c_2 - c_1)}$$

Strain

$$L_S = \frac{S_2}{S} = \frac{(c - c_1)}{f(c_2 - c_1)}$$

Electric field

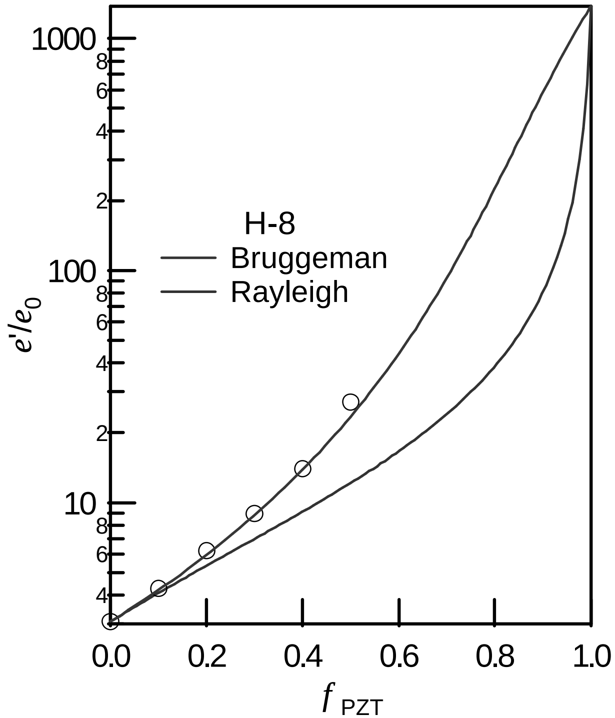
$$L_E = \frac{E_2}{E} = \frac{e - e_1}{f(e_2 - e_1)}$$

Electric displacement

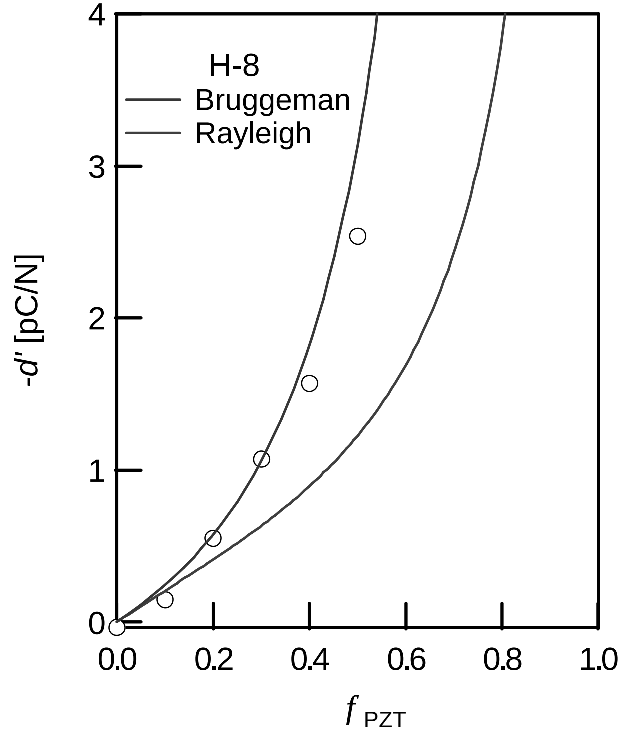
$$L_D = \frac{D_2}{D} = \frac{e_2(e - e_1)}{fe(e_2 - e_1)}$$

PZT / PVC Composite

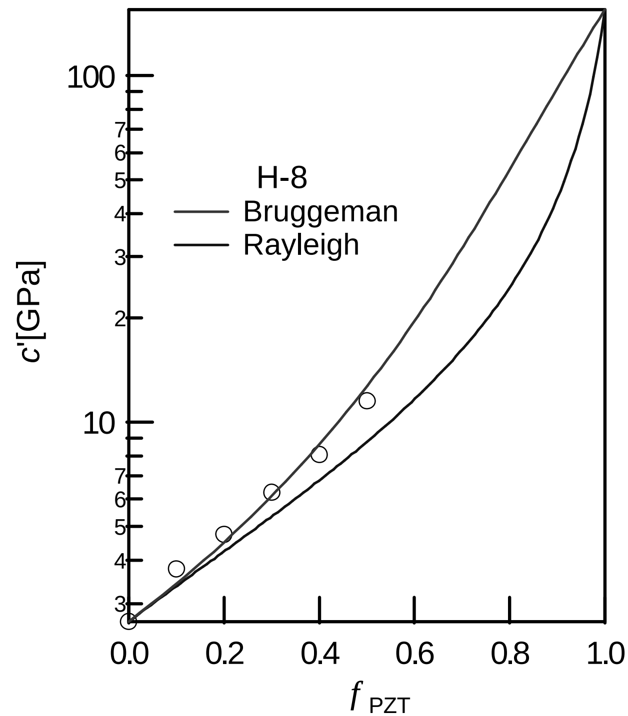
dielectric



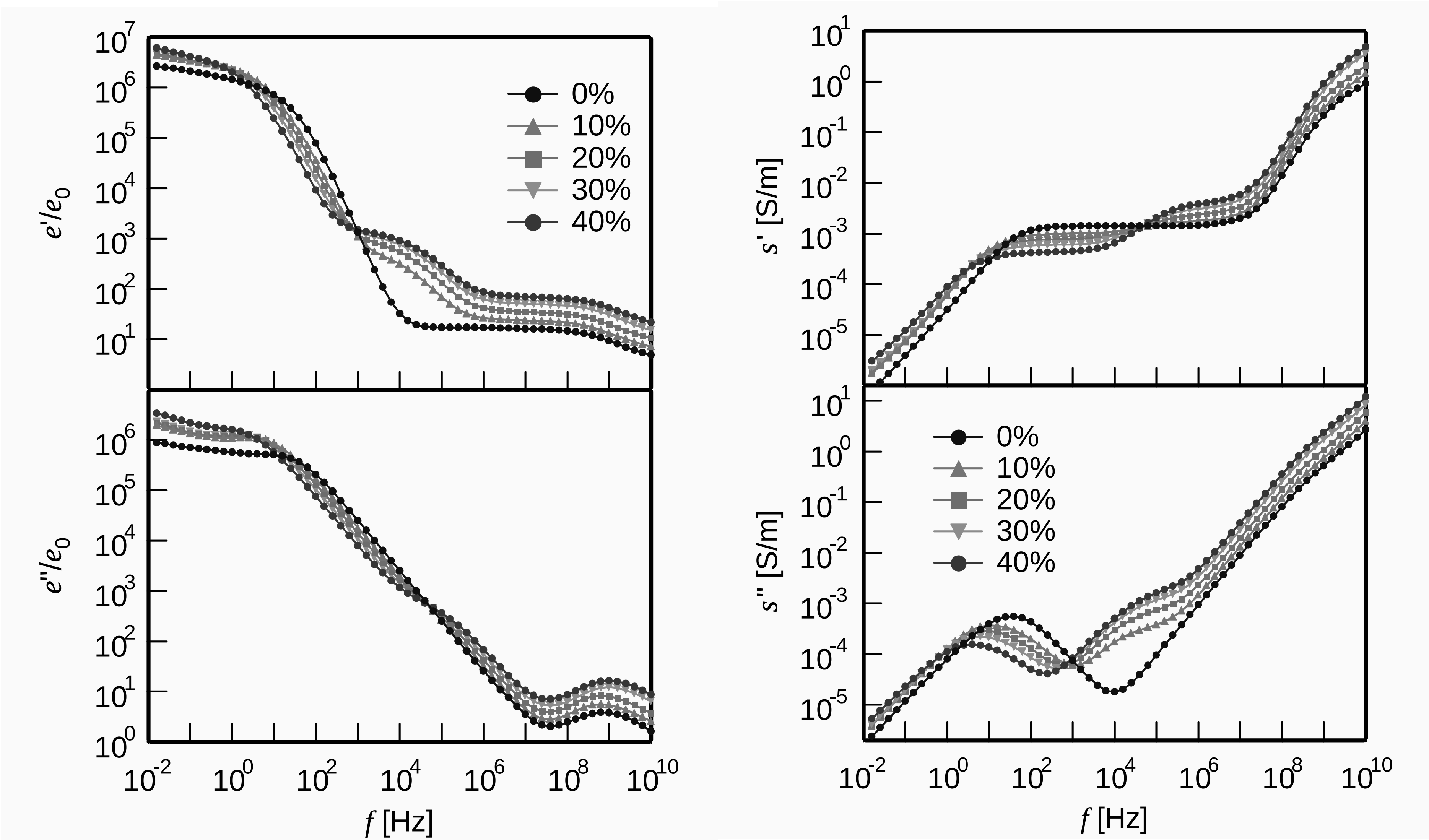
piezoelectric



elastic



Dielectric and Conductive Frequency Spectra for $BaTiO_3$(3mm)/PEO400 (0.1%$LiClO_4$) Composites



Dielectric and Conductive Processes in $BaTiO_3$ / Li-PEO Composites

$$e = e_{\infty} + \frac{\Delta e}{(1+(iwt_{\mathrm{seg}})^{b})^{a}}$$

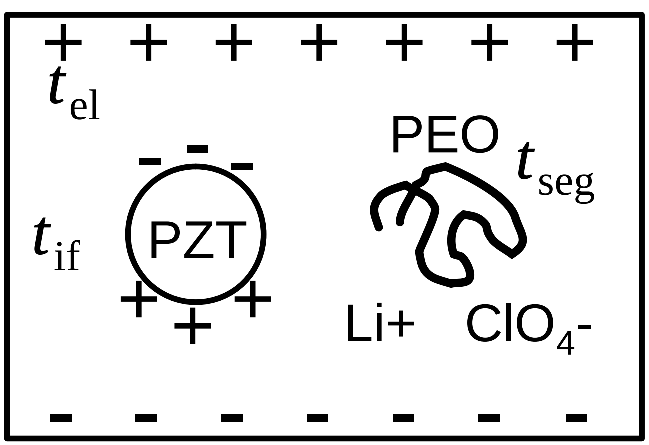
Segmental-mode Relaxation

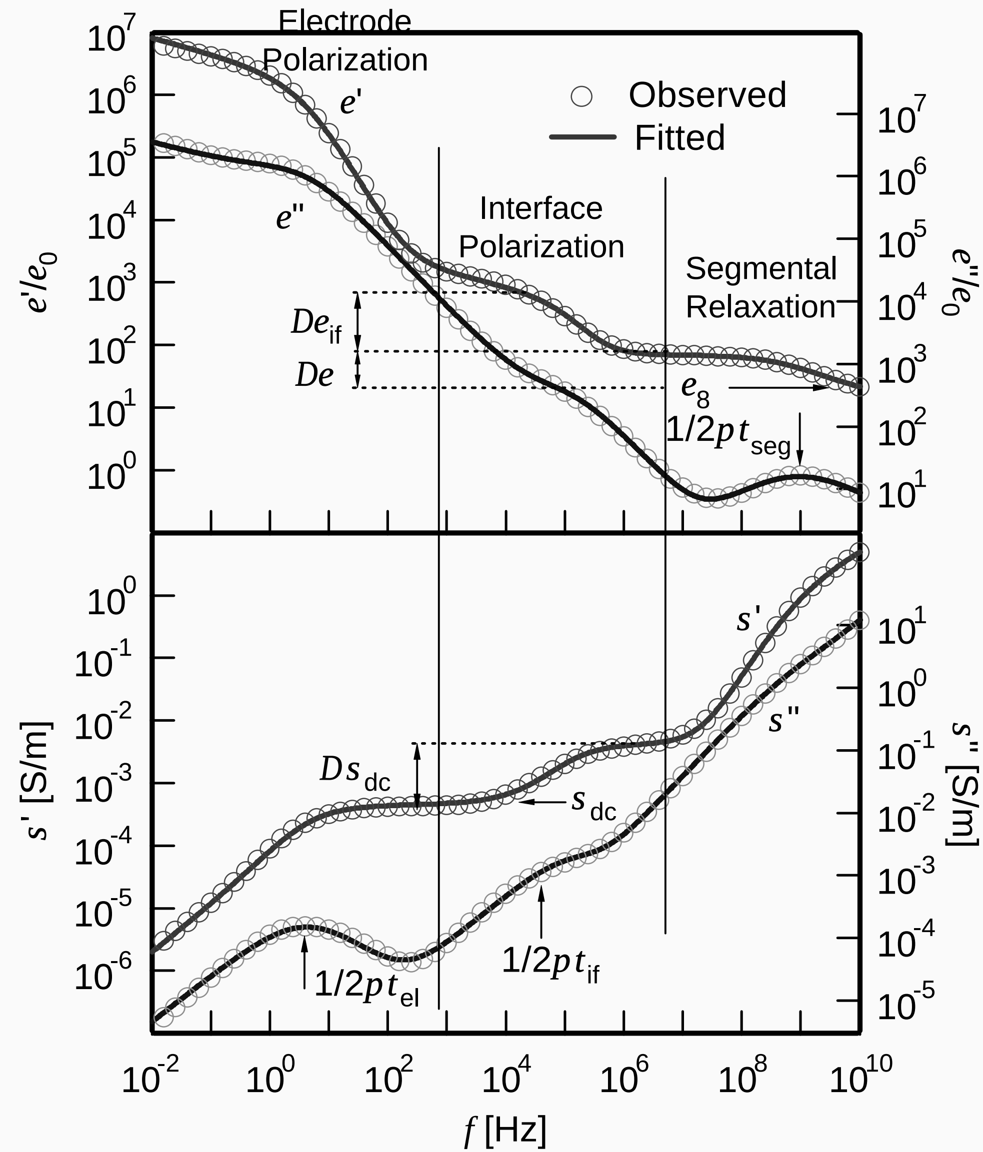
$$+\frac{\Delta s_{\mathrm{dc}}}{iw}\left(1-\frac{1}{1+(iwt_{\mathrm{if}})^{g_{\mathrm{if}}}}\right)$$

Interface Polarization

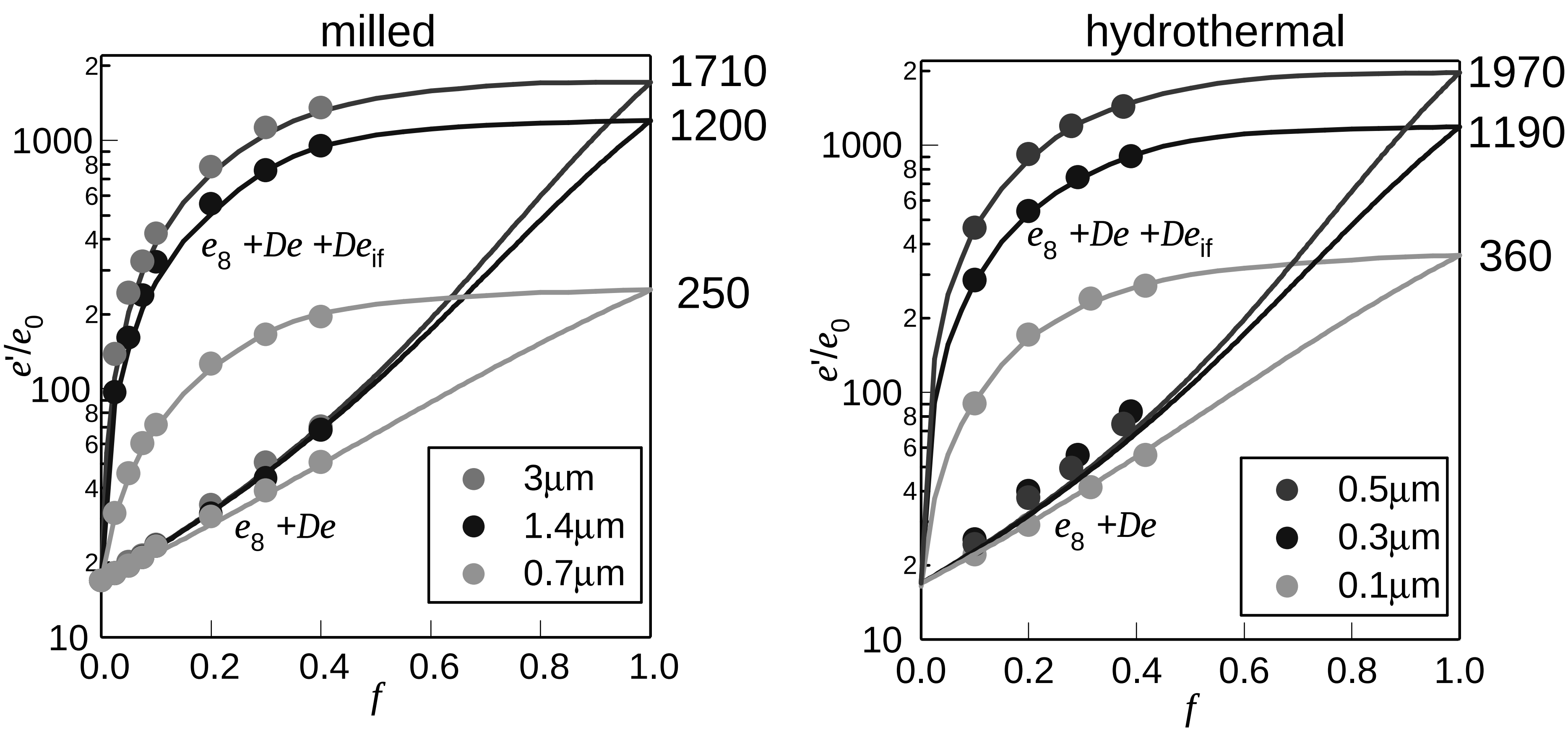
$$+\frac{s_{\mathrm{dc}}}{iw}\left(1-\frac{1}{1+(iwt_{\mathrm{el}})^{g_{\mathrm{el}}}}\right)$$

Electrode Polarization

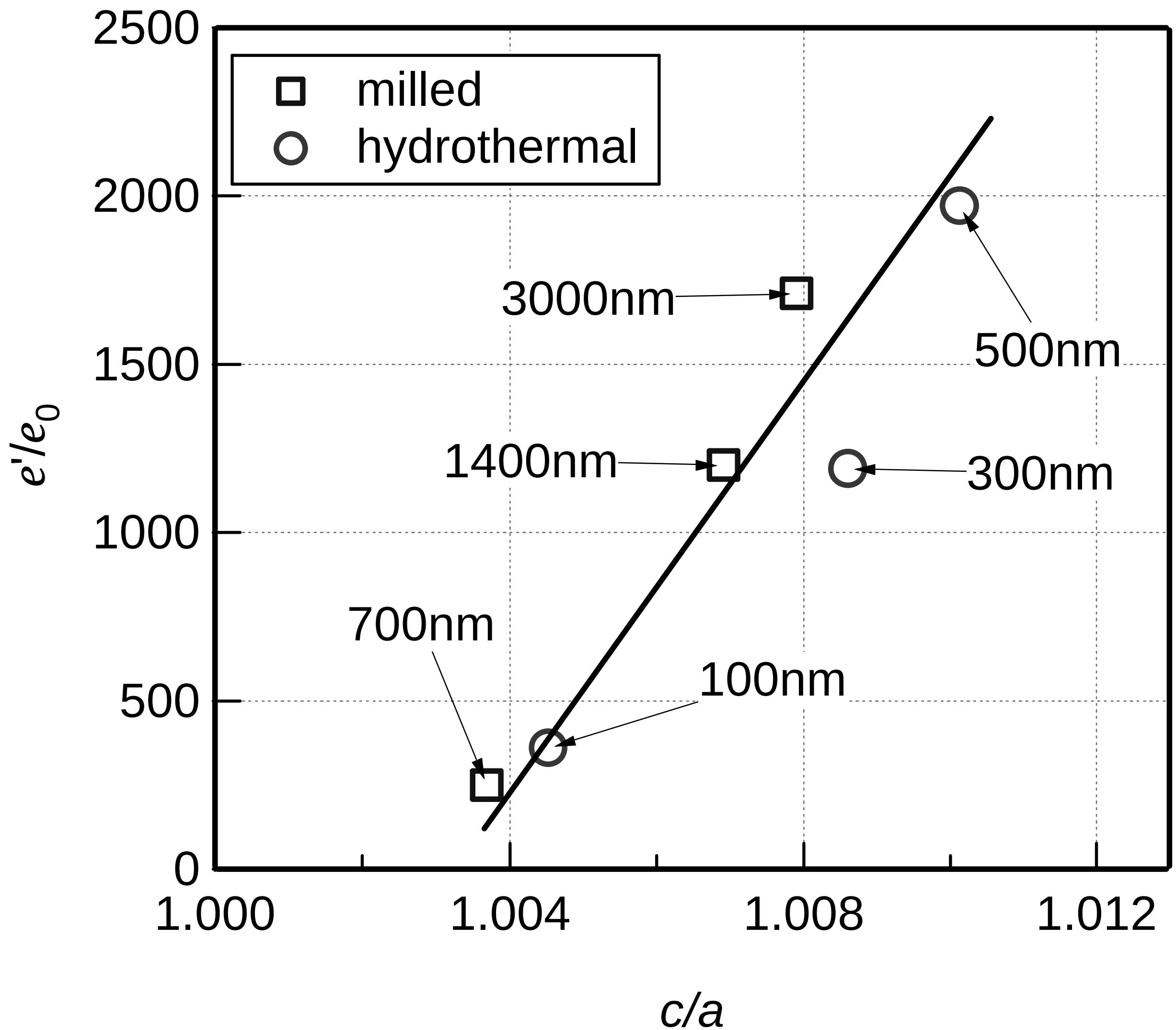




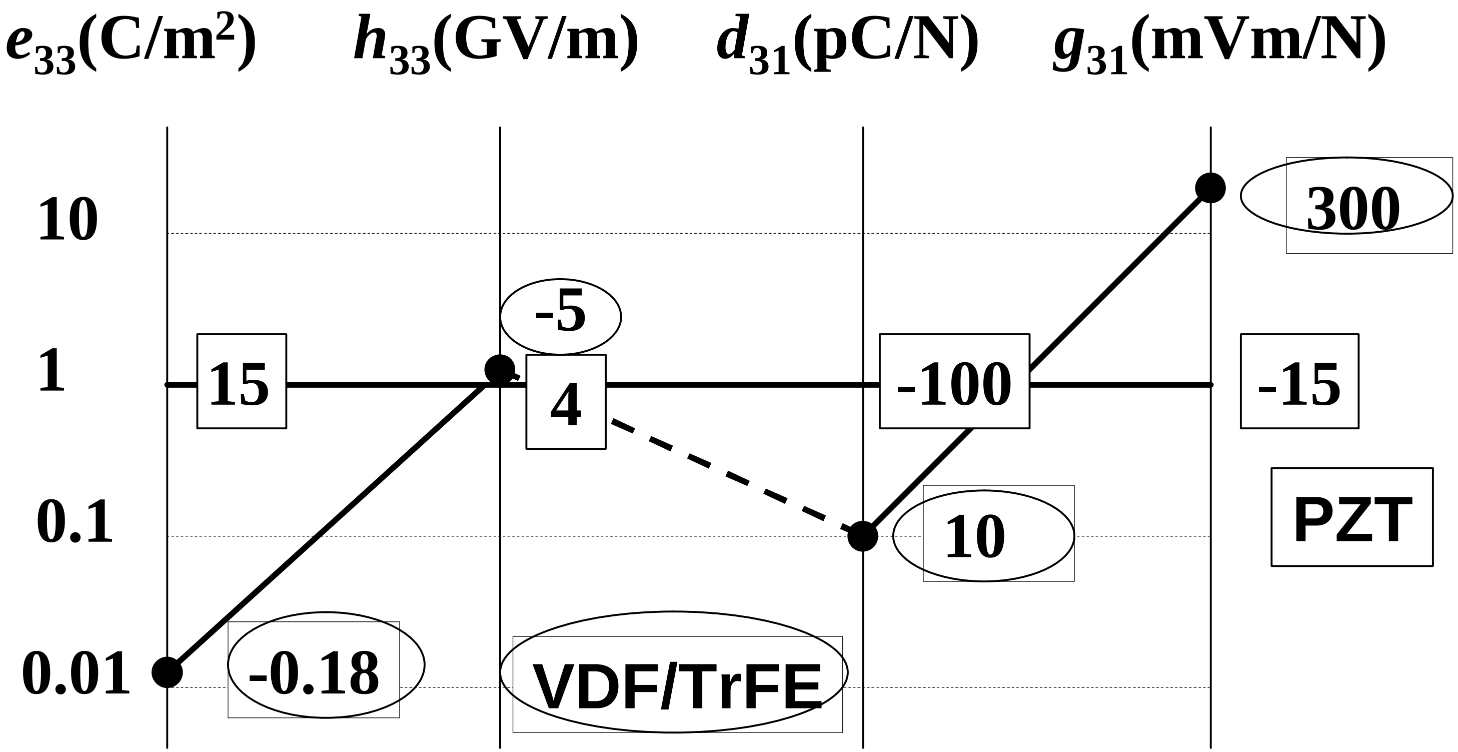
Dependence of observed and predicted permittivities on the volume fraction of $BaTiO_3$ with varying particle size



Relation between permittivity and *c/a* ratio for $BaTiO_3$ powder



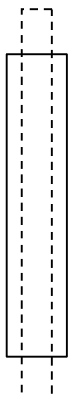
Comparison of Piezoelectric Constants of VDF/TrFE Copolymer and PZT Ceramics



Piezoelectric polymers are suited for sensors and soft actuators because of their low permittivity and high compliance.

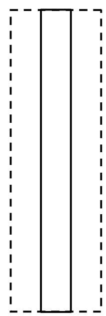
Deformation of Piezoelectric Polymers and Related Applications

Large Deformation, Low Power



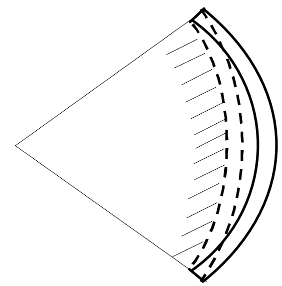
(A) Transverse Effect

Inch Worm



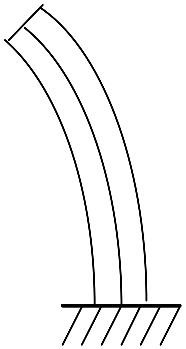
(B) Longitudinal Effect

Ultrasonic Transducer



(C) Longitudinal -Transverse Conversion

Speaker
Headphone



(D) Bimorph

Fan
Display